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(54) Title: PREPARATION OF METAL COORDINATION COMPLEX

(57) Abstract

Constrained geometry metal complexes that are useful in the preparation of catalysts for olefin polymerizations are prepared by contacting cyclopentadienyl compounds with metal compounds.

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PREPARATION OF METAL COORDINATION COMPLEX

The present invention relates to a method for preparing certain metal coordination complexes. More particularly the present invention relates to such a method that results in improved yields and simplified isolation of the metal complex.

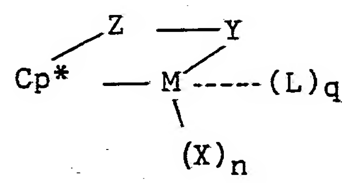
The metal coordination complexes to which the present process may be applied comprise a metal that is bound to a single cyclopentadienyl or substituted cyclopentadienyl group by both a η^5 bond and a divalent bridging group. These complexes are uniquely suited for use as catalysts in olefin polymerizations and to polymerize vinylaromatic monomers and olefins other than vinylaromatic monomers to prepare random copolymers useful as molding resins and in the preparation of films and foams for packaging or other applications.

Complexes and catalytic species that may be prepared according to the present invention, referred to as constrained geometry complexes, are disclosed in EP 416,815 and claimed in copending United States Patent Applications 545,403 and 547,728 both filed July 3, 1990, and assigned to the same assignee as the present application. The teachings of the foregoing pending United States Patent applications are hereby incorporated in their entirety by reference thereto. In the foregoing reference the metal complexes were prepared by reacting a metal compound such as $TiCl_4$ with a dilithiocyclopentadienylamidosilane or similar dianionic salt compound. Such salt compounds were prepared by reaction of an alkali metal cyclopentadienide or similar compound with a dichlorosilane followed by reaction with an amine or a lithium amide.

This reaction sequence has proven to be more complex and inefficient than is desired. In particular, incorporation of the cyclopentadienyl group into the desired structure early in the reaction sequence has proven undesirable because the synthetic sequence is apparently less efficient, and losses of the most expensive reagent are increased. Consequently, an improved synthesis of these commercially valuable catalyst components is desired.

Summary of the Invention

According to the present invention there is provided a process for preparing a metal coordination complex corresponding to the formula:



I

wherein:

M is a metal of Group 3-10, or the Lanthanide Series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl group, or a cyclopentadienyl group substituted with up to 4 moieties selected from the group consisting of hydrocarbyl, silyl, and germyl groups of up to 20 nonhydrogen atoms, halo and cyano moieties, or 2 adjacent carbons of the cyclopentadienyl group may be joined to the same C_{1-20} hydrocarbylene moiety;

Z is a moiety comprising boron, or a member of Group 14 or 15 of the Periodic Table of the Elements, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group having up to 30 non-hydrogen atoms or two X groups together may form a divalent derivative thereof;

n is 0, 1, 2, 3, or 4, and is 2 less than the valence of M

L is a neutral group associated with the complex with q being a rational number from 0 to 3; and

Y is an anionic ligand group bonded to Z and M comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system;

the said process comprising:

contacting a substituted cyclopentadiene compound corresponding to the formula: Cp*H-Z-YH;

wherein:

Cp*, Z, and Y are as previously defined,

either directly or indirectly with a metal compound corresponding to the formula: MX_mL_q, wherein M, X, L and q are as above defined, and m is equal to n + 2.

In the direct method the substituted cyclopentadiene compound is contacted with the metal compound corresponding to the formula:

MX_mL_q,

wherein X in at least two occurrences X is a hydride, amide or phosphide group,or a hydrocarbyl, or a hydrocarbyl group substituted with one or more halo, silyl, germyl, hydrocarbyloxy, amide, phosphide, sulfide, or siloxy groups.

In the indirect method, applicable where the metal compound corresponds to the formula, MX_mL_q, wherein X in at least 2 occurrences is halogen or hydrocarbyloxy, the substituted cyclopentadiene compound is first contacted with an alkali metal or alkaline earth metal or an organyl derivative thereof to form a metallated derivative, and thereafter said metallated derivative is contacted with the aforesaid metal compound.

In the event the substitution of the metal compound, MX_mL_q, satisfies the requirements for both the direct and indirect methods, either method may be employed.

Further according to the present invention there is also provided a process for preparing the above metal coordination complex of formula I, by the following steps:

1) contacting a halogenated compound of the formula: X'ZYH,

wherein Z and Y are as previously defined, and X' is halo,

with a metal cyclopentadienyl compound or a derivative thereof corresponding to the formula: $(X)_t(L)_sM'_uCp^*H$

wherein M' independently each occurrence is a metal selected from the group consisting of alkali metals, alkaline earth metals, Group 12 metals, Group 14 metals or metalloids, aluminum and copper; Cp*, X and L are as previously defined, and t, s, and u, independently each occurrence, are rational numbers from 0 to 3, to form the substituted cyclopentadiene compound corresponding to the formula:

Cp*H-Z-YH; and

2) thereafter, contacting the reaction product of step 1) with the aforementioned metal compound corresponding to the formula MX_mL_q, or first metallating the same with an alkali metal or alkaline earth metal or an organyl derivative thereof to form a metallated derivative, and contacting with the aforementioned halogenated metal compound of the formula MX_mL_q.

The process of the direct method involves the protonation of the X groups of the metal compound, by means of acidic hydrogen groups on the neutral aminocyclopentadienylsilane-, phosphinocyclopentadienylsilane- or similar ligand. Preferred metal compounds for use in the process include compounds wherein X is benzyl, neopentyl, trimethylsilylmethyl, or ring alkyl-, or amino- substituted benzyl compounds, such as 2-methylbenzyl and 2-dimethylaminobenzyl. A most preferred metal compound is tetrabenzyl titanium. Also preferably, M is titanium (IV) or zirconium (IV).

The process of the indirect method involves the displacement of the X groups of the metal compound by the metallated derivative. For such route X is preferably chlorine. Also preferably for this route, M is titanium (IV) or zirconium (IV).

Once having been prepared, if the metal of the metal coordination complex is not in its highest oxidation state and a higher oxidation state is desired, a noninterfering oxidizing agent may thereafter be contacted with the metal coordination complex to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the metal coordination complex and oxidizing agent, utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "noninterfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. Particularly suitable noninterfering oxidizing agents are AgCl, $PbCl_2$ or an organic halide such as methylene chloride. The reaction is preferably conducted in an inert solvent at a temperature from 0 to 50 °C.

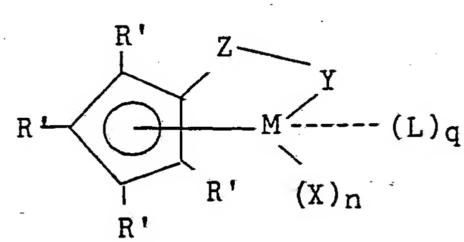
Detailed Description

All references herein to the Periodic Table of the Elements and to groups thereof shall refer to the version of the Table published in the Handbook of Chemistry and Physics, CRC Press (1987) utilizing the IUPAC convention for naming groups. Group 14 metals or metalloids are silicon, germanium, tin and lead.

Preferred C_{1-20} substituents on Cp* are alkyl or aryl groups of up to 10 carbons, especially methyl. Examples of suitable Cp* groups are cyclopentadienyl, tetramethylcyclopentadienyl, indenyl, and fluorenyl groups. When used herein, the terms cyclopentadienyl or cyclopentadienide, or similar terms will also be understood to refer generically to all such groups including the corresponding substituted derivatives as above defined.

Suitable neutral groups, L, include those bonded to the metal of the complex via a coordinate covalent bond as well as groups associated with the complex by van der Waals-, crystal packing-, or other bond. Examples include C_{1-12} ethers, including cyclic ethers, such as tetrahydrofuran, amines, and phosphines. Suitable metals M' include lithium, sodium, magnesium, aluminum, copper and zinc. Examples of suitable reagents, $(X)_t(L)_sM'_uCp^*H$, include: C_5H_5Li, $MgClC_5H_5$, $Mg(C_5H_5)_2$, $ClZnC_5H_5$, $Li((C_2H_5)_2O)_2Cu(CN)C_5H_5$, $(CH_3)_2AlC_5H_5$, $C_5H_5Si(CH_3)_3$ and the corresponding substituted cyclopentadienyl derivatives.

In a preferred embodiment the metal coordination complexes prepared according to the present invention correspond to the formula:



II

wherein R′ each occurrence is independently selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms or one or more R′ groups together may form a ring ;

X each occurrence independently is selected from the group consisting of hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, amide, phosphide, sulfide, siloxy groups, and combinations thereof having up to 20 non-hydrogen atoms;

Y is -O-, -S-, -NR*-, or -PR*-;

M is a Group 4 metal; and

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^* = CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, or BR^*;

wherein:

R* each occurrence is independently selected from the group consisting of hydrogen, cyano, halogen, hydrocarbyl, silyl, siloxy, and halogenated hydrocarbyl groups having up to 20 non-hydrogen atoms, and combinations thereof, or two or more R* groups from Z or from Y and Z form a fused ring system; and

n is 1 or 2.

Most preferred metal complexes are those wherein M is titanium or zirconium, Y is NR* and X, R*, and R′ independently each occurrence are selected from the group consisting of hydrogen, halo, silyl, hydrocarbyl and combinations thereof having up to 10 carbon or silicon atoms. Most highly preferably X in at least one occurrence is independently a C_{1-10} hydrocarbyl group or a C_{1-4} di-hydrocarbylamino- or C_{1-4} di-hydrocarbylphosphino-substituted hydrocarbyl group. Also most preferably, the metal cyclopentadienyl compounds or derivatives thereof used in step 1) are the lithium, sodium or potassium cyclopentadienides or tetramethylcyclopentadienides, and the alkali metal or alkaline earth metal or organyl derivative thereof of step 2) is potassium metal, methyl lithium, butyl lithium, phenyl lithium, isopropyl magnesium chloride, or methyl magnesium bromide.

Generally the reactions in either embodiment of the invention are conducted in a liquid diluent such as a C_{5-20} aliphatic or aromatic hydrocarbons, aliphatic ethers, and mixtures thereof. The reaction is conducted under an inert atmosphere. Nitrogen, helium or similar inert gas may be employed to produce the inert atmosphere. Agitation may be employed if desired. The temperature of each reaction is generally from -200°C to 200°C, preferably from -20°C to 150°C. The various reactants may be contacted for sevèral minutes up to several hours during the reactions of the invention.

The resulting complex may be rendered catalytically active by combining the same with an alumoxane such as methylalumoxane. Alternatively, in some cases catalytically active cationic derivatives of the neutral complexes produced by the process can be prepared by borane abstraction of an X group from the metal with, for example, trispentafluorophenyl borane. This technique involves contacting the metal coordination complex and borane compound in an inert solvent such as a C_{6-10} alkane at a temperature from -20°C to 200°C. The

method is more fully disclosed in copending application Serial Number 720,041, filed June 24, 1991 assigned to the same assignee as the present application. The teachings of the foregoing pending patent application are herein incorporated in their entirety by reference thereto.

Having described the invention the following examples are provided to further illustrate the same and are not to be construed as limiting. Unless stated to the contrary, parts and percentages are based on weight. Melt indices, I_2, are measured in accordance with ASTM D-1238 at 190°C using a weight of 2.16 Kg.

Example 1

A number of aminocyclopentadienyl silane derivatives were prepared for use in reacting with a Group 3-10 or Lanthanide metal compound.

Preparation 1:

(N-t-butylamino)(dimethyl)(2,3,4,5-tetramethylcyclopentadienyl)silane

To a solution of 0.200 g (1.39 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 8 mL tetrahydrofuran (THF) under a nitrogen atmosphere was added 0.2299 g (1.39 mmol) (N-t-butylamino)(chloro)dimethylsilane. The reaction mixture was stirred several hours. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil. The yield was 0.3028 g (86.8 percent).

Preparation 2:

(N-t-butylamino)(dimethyl)(cyclopentadienyl)silane

To a solution of 0.250 g lithium cyclopentadienide (contains 9-10 mole percent lithium methyl cyclopentadienide) (total 3.41 mmol) in 6 mL THF was added 0.5752 g (3.47 mmol) (N-t-butylamino)(chloro)dimethylsilane. The reaction mixture was stirred several hours. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed in vacuo to give the product as a pale yellow oil. The yield was 0.4675 g (70.0 percent).

Preparation 3:

(N-t-butylamino)(dimethyl)(cyclopentadienyl)silane

To a solution of 1.50 g (9.05 mmol) (N-t-butylamino)(chloro)dimethylsilane in 40 mL THF was added dropwise 4.5 mL of a 2.0 M solution of sodium cyclopentadienide in THF over a 20 minute period. The reaction mixture was stirred several hours. Monitoring by gas-liquid chromatography (GC) indicated clean formation of the product. The solvent was removed, the residue was extracted with diethyl ether and filtered. The ether was removed in vacuo to give the product as a pale yellow oil. The yield was 1.44 g (81 percent).

Preparation 4:

(N-t-butylamino)(dimethyl)(methylcyclopentadienyl)silane

2.300 g sodium methylcyclopentadienide (22.5 mmol) was reacted with 3.733 g (22.5 mmol) (N-t-butylamino)(chloro)dimethylsilane in 92 mL THF. The reaction mixture was

stirred several hours. Monitoring by GC indicated that the reaction was complete. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed in vacuo to give the product as a colorless oil. The yield was 3.814 g (81.0 percent).

Preparation 5:

(N-t-butylamino)(dimethyl)(t-butylcyclopentadienyl)silane

To a solution of 3.346 g (20.2 mmol) (N-t-butylamino)(chloro)dimethylsilane in 75 mL THF was added 3.577 g (17.7 mmol) lithium t-butylcyclopentadienide etherate. Lithium t-butylcyclopentadienide was prepared by contacting methyl lithium with 6,6-dimethylfulvene. The reaction mixture was stirred several hours. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed in vacuo to give the product as a pale yellow oil. The yield was 2.873 g (64.6 percent).

Preparation 6:

(N-t-butylamino)(chloro)diphenylsilane

To a solution of 12.66 g (50.0 mmol) dichlorodiphenylsilane in 220 mL pentane was added 7.38 g (101 mmol) t-butyl amine. Thick precipitate formed. The reaction mixture was stirred overnight, then filtered. The pentane was removed in vacuo to give the product as a viscous colorless oil. The yield was 13.55 g (93.5 percent). ^1H (C_6D_6) δ 7.85 (m, 4H), 7.14 (m, 6H), 1.51 (s, 1H), 1.10 (s, 9H). ^{13}C (C_6D_6) δ 135.8, 134.9, 130.6, 128.2, 50.8, 33.2.

(N-t-butylamino)(diphenyl)(2,3,4,5-tetramethylcyclopentadienyl)silane

To a solution of 4.7023 g (16.2 mmol) (N-t-butylamino)(chloro)diphenylsilane in 130 mL THF was added a solution of 2.409 g (16.7 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 40 mL THF. The reaction mixture was stirred overnight. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed in vacuo to give the product as a creamy white solid which could be recrystallized from pentane at low temperature. The yield was 5.982 g (98.2 percent).

Preparation 7:

(N-t-butylamino)(dimethyl)(tetrahydrofluorenyl)silane

To a solution of 0.37 g (2.2 mmol) of (N-t-butylamino)(chloro)dimethylsilane in 30 mL of THF was added over a 15 minute period a 10 mL THF solution containing 0.39 g (2.2 mmol) of lithium tetrahydrofluorenide prepared by the lithiation of tetrahydrofluorene with n-butyl lithium. The tetrahydrofluorene in turn may be prepared according to the procedure described in J. Org. Chem. 55, p 5301-5302, (1990). The solution was allowed to stir for 5 hours for completion as shown by GC analysis. The solvent was then removed, the residue extracted with pentane and filtered. The pentane was then removed under reduced pressure to give the product as a light-yellow oil. The yield was 0.55 g (83 percent). ^1H NMR (THF-d_8) δ7.0-7.4 (m, 4H), 1.5-2.7 (m, 8H), 1.15 (s, 9H), 0.10 (s, 3H), -0.14 (s, 3H). MS : 299

Preparation 8:

(N-t-butylamino)(dimethyl)(indenyl)silane

To a solution of 0.54 g (3.3 mmol) of (N-t-butylamino)(chloro)dimethylsilane in 50 mL of diethyl ether was added a 10 mL diethyl ether solution containing 0.40 g (3.28 mmol) of lithium indenide over a 1 hour period. The solution was allowed to stir for 24 hours for completion as shown by GC analysis. The solvent was then removed, the residue extracted with pentane and filtered. The pentane was then removed under reduced pressure to give the product as a light-yellow oil. The yield was 0.58 g (83 percent). The product's identity was confirmed by gas/liquid chromatography and mass spectroscopy.

Preparation 9:

(N-t-butylamino)(dimethyl)(octahydrofluorenyl)silane

To a solution of 0.46 g (2.76 mmol) of (N-t-butylamino)(chloro)dimethylsilane in 80 mL of THF was added 0.50 g (2.76 mmol) of lithium octahydrofluorenide. The lithium octahydrofluorenide was prepared by the lithiation of octahydrofluorene with n-butyl lithium. The suspension was then brought to reflux for 5 minutes with consequent dissolution of the solids. After this time period the solution was allowed to cool to room temperature, GC analysis showed the reaction to be complete. The solvent was then removed, the residue extracted with pentane and filtered. The pentane was then removed under reduced pressure to give the product as a light-yellow oil. The yield was 0.73 g (92 percent). ^{1}H NMR (C_6D_6) δ2.8-1.5 (m, 16H), 1.13 (s, 9H), 0.16 (s, 6H). MS:303

Preparation 10:

(N-t-butylamino)(dimethyl)(1-methylindenyl)silane

To a solution of 1.82 g (11.0 mmol) of (N-t-butylamino)(chloro)dimethylsilane in 25 mL of diethyl ether was added a 20 mL diethyl ether solution containing 1.50 g (11.0 mmol) of lithium 1-methylindenide over a 30 minute period. Lithium 1-methyl indenide was prepared by the lithiation of 1-methyl indene with n-butyl lithium. 1-methyl indene in turn can be prepared according to the procedures disclosed in J. Org. Chem. 47, p 1051-1058, (1982). The solution was allowed to stir for 5 hours for completion as shown by GC analysis. The solvent was then removed, the residue extracted with pentane and filtered. The pentane was then removed under reduced pressure to give the product as a light-yellow oil. The yield was 2.1 g (73 percent). ^{1}H NMR (THF-d_8) δ7.15 (d, 1H), 7.31 (d, 1H), 7.12 (m, 2H), 6.33 (s, 1H), 3.4 (m, 1H), 2.18 (s, 3H), 1.19 (s, 9H), 0.10 (s, 3H), 0.13 (s, 3H). MS: 259

Preparation 11:

(N-t-butylamino)(dimethyl)(2,3,4,5-tetramethylcyclopentadienyl)silane

To a solution of 3.758 g (26.1 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 120 mL THF was added 4.3195 g (26.1 mmol) (N-t-butylamino)(chloro)dimethylsilane. The reaction mixture was stirred overnight. The solvent was removed, the residue was extracted

with pentane and filtered. The pentane was removed in vacuo to give the product as a light-yellow oil. The yield was 6.4244 g (98.0 percent).

Preparation 12:

t-Butylamino(chloromethyl)dimethylsilane

9.56 g (131 mmol) t-butylamine and 9.35 g (65.3 mmol) chloro(chloromethyl)dimethylsilane were combined in 120 mL ether. Thick precipitate formed. The reaction mixture was stirred several days, then filtered. The ether was removed in vacuo to give the product as a colorless liquid. Yield: 6.425 g, 54.7 percent. ^1H (C_6D_6) δ 2.57 (s, 2H), 0.99 (s, 9H), 0.54 (s, 1H), 0.11 (s, 6H). ^{13}C (C_6D_6) 49.3, 33.7, 32.4, -1.1.

(N-t-butylamino)(dimethyl)((2,3,4,5-tetramethylcyclopentadienyl)methyl)silane

A solution of 2.432 g (16.9 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 30 mL THF was added to 3.032 g (16.9 mmol) t-butylamino(chloromethyl)dimethylsilane. Precipitate formed slowly and the reaction mixture was stirred overnight. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed in vacuo to give the product as a light-yellow oil. The yield was 2.988 g (66.7 percent).

Preparation 13:

(2-methoxyphenyl)amino)dimethyl(tetramethylcyclopentadienyl)silane)

To 1.3 g (5.9 mmol) ((tetramethylcyclopentadienyl)dimethylsilyl)chloride in 50 mL tetrahydrofuran (THF) was added 0.86 g (5.9 mmol) sodium 2-methoxyanilide. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue extracted with pentane. The pentane extracts were filtered, combined, and concentrated to give a pale yellow liquid. Yield 1.4 g (79 percent). ^1H NMR (benzene-d_6) δ 6.91 (m, 2.2), 6.74 (m, 1.1), 6.57 (d, 1.1, J = 9), 4.25 (s, 1), 3.32 (s, 3.7), 1.93 (s,6.7), 1.80 (s, 6.8), 0.13 (s, 6.3).

Preparation 14:

((4-fluorophenyl)amino)dimethyl(tetramethylcyclopentadienyl)silane

Equimolar quantities of ((tetramethylcyclopentadienyl)dimethylsilyl)chloride and lithium 4-fluorophenyl anilide were combined in THF and the mixture stirred overnight. The solvent was removed under reduced pressure. ^1H NMR (benzene-d_6) δ 6.79 (m, 2.5), 6.33 (m, 2.4), 2.95 (s,1), 2.90 (s, 1), 1.87 (s, 6.9), 1.79 (s, 6.9), 0.02 (s, 5.8).

COMPLEX PREPARATION

Example 1:

Dilithium (tert-butylamido)(dimethyl)(tetramethylcyclopentadienyl)silane

To a solution of 3.000 g (11.98 mmol) of the neutral ligand $HN\text{-}t\text{-}BuSiMe_2C_5Me_4H$ of Preparation 1 in 100 mL ether was slowly added 9.21 mL of 2.6 M (23.95 mmol) butyl lithium in mixed C_6 alkane solvent. A white precipitate formed and the reaction mixture was stirred overnight, then filtered. The solid was washed several times with ether then dried under reduced pressure to give the product as a white powder. The yield was 3.134 g (99.8 percent).

(Tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane titanium dichloride

0.721 g (3.80 mmol) Of $TiCl_4$ was added to 30 mL frozen (-196°C) THF. The mixture was allowed to warm to -78°C (dry ice bath). To the resulting yellow solution was slowly added a solution of 1.000 g (3.80 mmol) dilithium (tert-butylamido)(dimethyl)tetramethylcyclopentadienyl)silane in 30 mL THF. The solution was allowed to warm to room temperature while stirring overnight. The solvent was removed from the resulting very dark solution. The residue was extracted with pentane and filtered. Cooling in a freezer caused the separation of a very soluble dark reddish-brown material from a light yellow-green crystalline solid. The solid was filtered out and recrystallized from pentane to give the olive-green product. The yield was 0.143 g, 10.2 percent.

Example 2:

Dilithium (N-t-butylamido)(2,3,4,5-tetramethylcyclopentadienyl)(diphenyl)silane

To a solution of 5.982 g (15.93 mmol) (N-t-butylamino)(2,3,4,5-tetramethylcyclopentadienyl)(diphenyl)silane (Preparation 6) in 100 mL ether was slowly added 22.06 mL of 1.48 M (32.65 mmol) butyl lithium in mixed hexane solvent. The resulting yellow solution was stirred overnight, then filtered from a small amount of precipitate and the solvent was removed. The solid was slurried in pentane, filtered and washed with pentane, then dried in vacuo to give the product as a white powder as a 0.5 diethyl ether solvate (by NMR). The yield was 6.784 (100 percent). ^1H (not including solvate peaks) (THF d-8) δ 7.78 - 7.19 (3 m, 10H), 1.93 (s, 6H), 1.83 (s, 6H), 1.08 (s, 9H).

[(N-t-butylamido)(diphenyl)(tetramethyl-η^5-cyclopentadienyl)silane]titanium dichloride

A flask was charged with 0.7701 g (1.99 mmol) dilithium (N-t-butylamido)(2,3,4,5-tetramethylcyclopentadienyl)(diphenyl)silane and 0.7365 g (1.99 mmol) $TiCl_3(THF)_3$. To this was added 80 mL THF. After the solution was stirred for 10 minutes, 0.3040 g (1.09 mmol) $PbCl_2$ was added and the solution was stirred for several hours. The initially deep brown-black solution turned orange-red. The solution was filtered and the solvent was removed. The residue was extracted with pentane and filtered and the solvent was removed to give a glassy yellow solid. The compound was purified by slurrying in pentane and collecting on a filter and drying under vacuum. The yield of lemon-yellow colored powder was 0.3054 g, 31.2 percent ^1H (C_6D_6) 7.84 - 7.81 (m, 4H), 7.19 - 7.17 (m, 6H), 1.95 (s, 6H), 1.81 (s, 6H), 1.67 (s, 9H) ^{13}C (C_6D_6) 142.8, 138.8, 136.3, 135.6, 130.6, 128.3, 104.6, 62.0, 33.5, 17.1, 13.1.

Example 3:

Dilithium (N-t-butylamido)(dimethyl)((2,3,4,5-tetramethylcyclopentadienyl)methyl)silane

To a solution of 2.988 g (11.3 mmol) (N-t-butylamino)(dimethyl)((2,3,4,5-tetramethylcyclopentadienyl)methyl)silane (Preparation 12) in 70 mL ether was slowly added 15.90 mL of 1.416 M (22.5 mmol) butyl lithium in hexanes under gas evolution. The resulting yellow solution was stirred overnight and the solvent was removed from the pale orange solution. The resulting solid was slurried in pentane, filtered and washed with pentane, then dried in vacuo to give the product as a light orange powder in essentially quantitative yield.

[(N-t-butylamido)(dimethyl)(tetramethyl-η5-cyclopentadienylmethyl)silane]titanium dichloride

A flask was charged with 2.018 g (7.27 mmol) dilithium (N-t-butylamido)(dimethyl)(2,3,4,5-tetramethylcyclopentadienylmethyl)silane and 2.696 g (7.27 mmol) $TiCl_3(THF)_3$. To this was added 70 mL THF. After the solution was stirred for 10 minutes, 1.062 g (3.81 mmol) $PbCl_2$ was added to the very dark solution and the reaction mixture was stirred overnight. The deep red-brown solution was filtered and the solvent was removed. The residue was extracted with pentane and filtered. After concentration, the solution was cooled in a -35°C freezer to induce crystallization. The product was recrystallized twice from pentane. Yield of bright red crystalline product was 0.6565 g, 23.6 percent ^1H (C_6D_6) δ 2.06 (s, 6H), 1.94 (s, 6H), 1.89 (s, 2H), 1.58 (s, 9H), 0.30 (s, 6H) ^{13}C (C_6D_6) δ 132.8, 131.8, 128.4, 62.5, 33.4, 17.5, 13.9, 13.5, 7.6.

Example 4:

(N-t-butylamido)dimethyl(tetramethyl-η5-cyclopentadienyl)silanetitanium dibenzyl

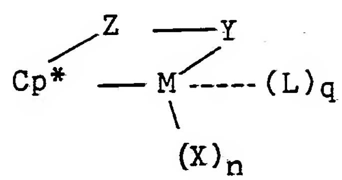
In an inert atmosphere dry box titanium tetrabenzyl (0.328 g, 0.8 mmol) was loaded into a 100 ml flask and dissolved into 40 ml dry, degassed pentane. To this solution was added 0.2 g (0.8 mmol) of the neutral ligand, (N-t-butylamino)(dimethyl)(2,3,4,5-tetramethylcyclopentadienyl)silane, of Preparation 1. The reaction flask was placed in an oil bath at 55-60°C for 12 hours. After heating, the solvent was removed under reduced pressure giving (N-t-butylamido)dimethyl(tetramethyl-η5-cyclopentadienyl)silanetitanium dibenzyl. Yield was 90 percent based upon spectroscopic data. Further purification is accomplished by recrystallization from pentane. ^1H NMR, (C_6D_6, ppm): 7.18-6.90 (m, C_6H_5, 10H); 2.581, 2.249 (AB, $CH_2C_6H_5$, 4H, J_{HH} = 8 Hz); 1.806, 1.631 (s, $C_5(CH_3)_4$, 6H each); 1.426.

Polymerization

A stainless steel shot tank was charged with 500 µL (5.0 µmol) of a 0.010 M toluene solution of (tert-butylamido)dimethyl(tetramethyl-η5-cyclopentadienyl)silanetitanium dichloride and 2.5 mL of toluene in an argon filled glove box. In a second shot tank, 5.0 mL of a 1.0 M solution of methylalumoxane (MAO) cocatalyst in toluene was added to 92 mL of toluene. Both shot tanks were sealed, removed from the glove box and attached to a 600 mL pressure vessel. The pressure vessel was evacuated and flushed with argon and then flushed with ethylene. The cocatalyst solution was added to the pressure vessel and the contents heated to 89°C under an ethylene pressure of 620 kPa (90 psig). The catalyst solution was added to the reactor at this time. The temperature rose to 109°C within seconds as a result of an exothermic reaction. The ethylene pressure was regulated between 1241-1275 kPa (180-185 psig). After about 0.5 hours the reactor temperature had increased to about 110°C and the uptake of ethylene increased. After 1.0 hours ethylene feed was discontinued, the reactor was vented to the atmosphere, and allowed to cool. The pressure vessel was opened, quenched with methanol, and the polymer was isolated. After removing the volatile components, the yield of crystalline polyethylene was 24 g.

Claims:

1. A process for preparing a metal coordination complex corresponding to the formula:



wherein:

M is a metal of Group 3-10, or the Lanthanide Series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl group, or a cyclopentadienyl group substituted with up to 4 moieties selected from the group consisting of hydrocarbyl, silyl, and germyl groups of up to 20 nonhydrogen atoms, halo and cyano moieties, or 2 adjacent carbons of the cyclopentadienyl group may be joined to the same C_{1-20} hydrocarbylene moiety;

Z is a moiety comprising boron, or a member of Group 14 or 15 of the Periodic Table of the Elements, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group having up to 30 non-hydrogen atoms or two X groups together may form a divalent derivative thereof;

n is 0, 1, 2, 3, or 4, and is 2 less than the valence of M

L is a neutral group associated with the complex with q being a rational number from 0 to 3; and

Y is an anionic ligand group bonded to Z and M comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system;

the said process comprising:

contacting a substituted cyclopentadiene compound corresponding to the formula: Cp*H-Z-YH;

wherein:

Cp*, Z, and Y are as previously defined,

either directly or indirectly with a metal compound corresponding to the formula: MX_mL_q, wherein M, X, L and q are as above defined, and m is equal to n + 2.

2. A process according to Claim 1 wherein the substituted cyclopentadiene compound is prepared by contacting a halogenated compound of the formula: X'ZYH, wherein Z and Y are as previously defined, and X' is halo, with a metal cyclopentadienyl compound or a derivative thereof corresponding to the formula: $(X)_t(L)_sM'_uCp^*H$, wherein M' independently each occurrence is a metal selected from the group consisting of alkali metals, alkaline earth metals, Group 12 metals, Group 14 metals or metalloids, aluminum, and copper; and Cp*, X and L are as defined in Claim 1, and t, s, and u, independently each occurrence, are rational numbers from 0 to 3, to form the substituted cyclopentadiene compound.

3. A process according to Claim 1 wherein the substituted cyclopentadiene compound is directly contacted with a metal compound corresponding to the formula:

MX_mL_q,

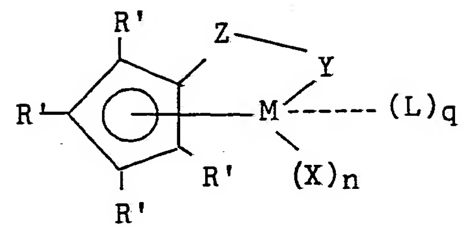
wherein X independently each occurrence is an anionic ligand group and in at least two occurrences X is a hydride, amide or phosphide group,or a hydrocarbyl, or a hydrocarbyl group substituted with one or more halo, silyl, germyl, hydrocarbyloxy, amide, phosphide, sulfide, or siloxy groups to form the metal coordination complex.

4. A process according to Claim 1 wherein the substituted cyclopentadiene compound is indirectly contacted with a metal compound corresponding to the formula: MX_mL_q, wherein X in at least 2 occurrences is halogen or hydrocarbyloxy, by first contacting the substituted cyclopentadiene compound with an alkali metal or alkaline earth metal or an organyl derivative thereof to form a metallated derivative, and thereafter contacting such metallated derivative with the metal compound to form the metal coordination complex.

5. A process according to Claim 4 wherein the substituted cyclopentadiene compound is metallated to form a metallated derivative by contacting with potassium metal, butyl lithium, methyl lithium, phenyl lithium, isopropyl magnesium chloride, or methyl magnesium bromide.

6. A process according to Claim 1 wherein Y is NR* where R* independently each occurrence is selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof.

7. A process according to Claim 1 wherein the metal coordination complex corresponds to the formula:



wherein R' each occurrence is independently selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms or one or more R' groups together may form a ring ;

X each occurrence independently is selected from the group consisting of hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, amide, phosphide, sulfide, siloxy and combinations thereof having up to 20 non-hydrogen atoms;

Y is -O-, -S-, -NR*-, or -PR*-;

M is a Group 4 metal; and

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^* = CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, or BR^*;

wherein:

R* each occurrence is independently selected from the group consisting of hydrogen, cyano, halogen, and hydrocarbyl, silyl, siloxy, and halogenated hydrocarbyl groups having up to 20 non-hydrogen atoms, and combinations thereof, or two or more R* groups from Z, or both Y and Z form a fused ring system;

n is 1 or 2; and

L is a neutral group associated with the complex with q being a rational number from 0 to 3.

8. A process according to Claim 7 wherein X each occurrence is a C_{1-10} hydrocarbyl group or a C_{1-4} di-hydrocarbylamino- or C_{1-4} di-hydrocarbylphosphino-substituted derivative thereof.

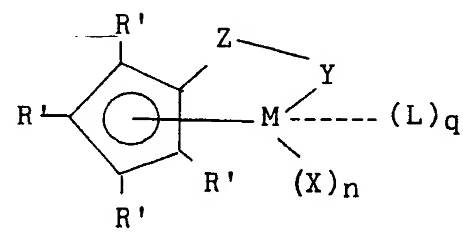
9. A process according to Claim 7 wherein M is titanium or zirconium.

10. A process according to Claim 9 wherein the metal coordination complex is (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane zirconium dichloride, (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane titanium dichloride, (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane zirconium dibenzyl, or (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)-silane titanium dibenzyl.

AMENDED CLAIMS

[received by the international Bureau on 29 January 1993 (29.01.93); original claims 1,3 and 4 amended; other claims unchanged (3 pages)]

1. A process for preparing a metal coordination complex corresponding to the formula:



wherein R′ each occurrence is independently selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms or one or more R′ groups together may form a ring;

X each occurrence independently is selected from the group consisting of hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, amide, phosphide, sulfide, siloxy and combinations thereof having up to 20 non-hydrogen atoms, and C_{1-4} di-hydrocarbylamino- or C_{1-4} di-hydrocarbylphosphino-substituted C_{1-10} hydrocarbyl groups;

Y is -O-, -S-, -NR*-, or -PR*-;

M is a Group 4 metal; and

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^* = CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, or BR^*;

wherein:

R* each occurrence is independently selected from the group consisting of hydrogen, cyano, halogen, and hydrocarbyl, silyl, siloxy, and halogenated hydrocarbyl groups having up to 20 non-hydrogen atoms, and combinations thereof, or two or more R* groups from Z, or both Y and Z form a fused ring system;

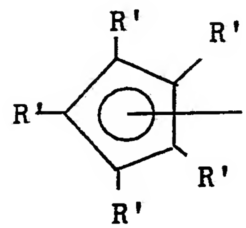
n is 1 or 2; and

L is a neutral group associated with the complex with q being a rational number from 0 to 3;

said process comprising:

contacting a substituted cyclopentadiene compound corresponding to the formula: $Cp^*H\text{-}Z\text{-}YH$;

wherein:

Cp* is  , and Z and Y are as previously defined,

either directly or indirectly with a metal compound corresponding to the formula: MX_mL_q, wherein M, X, L and q are as above defined, and m is equal to n + 2.

2. A process according to Claim 1 wherein the substituted cyclopentadiene compound is prepared by contacting a halogenated compound of the formula: X'ZYH, wherein Z and Y are as previously defined, and X' is halo, with a metal cyclopentadienyl compound or a derivative thereof corresponding to the formula: $(X)_t(L)_sM'_uCp^*H$, wherein M' independently each occurrence is a metal selected from the group consisting of alkali metals, alkaline earth metals, Group 12 metals, Group 14 metals or metalloids, aluminum, and copper; and Cp*, X and L are as defined in Claim 1, and t, s, and u, independently each occurrence, are rational numbers from 0 to 3, to form the substituted cyclopentadiene compound.

3. A process according to Claim 1 wherein the substituted cyclopentadiene compound is directly contacted with the metal compound corresponding to the formula:

MX_mL_q,

wherein M, m, L, and q are as previously defined; and

X independently each occurrence is an anionic ligand group and in at least two occurrences X is a hydride, amide or phosphide group, or a hydrocarbyl group, or a hydrocarbyl group substituted with one or more halo, silyl, germyl, hydrocarbyloxy, amine, phosphine, sulfide, or siloxy groups to form the metal coordination complex.

4. A process according to Claim 1 wherein the substituted cyclopentadiene compound is indirectly contacted with a metal compound corresponding to the formula:

MX_mL_q,

wherein M, m, L, and q are as previously defined; and

X in at least 2 occurrences is halogen or hydrocarbyloxy,

by first contacting the substituted cyclopentadiene compound with an alkali metal or alkaline earth metal or an organyl derivative thereof to form a metallated derivative, and thereafter contacting such metallated derivative with the metal compound to form the metal coordination complex.

5. A process according to Claim 4 wherein the substituted cyclopentadiene compound is metallated to form a metallated derivative by contacting with potassium metal,

butyl lithium, methyl lithium, phenyl lithium, isopropyl magnesium chloride, or methyl magnesium bromide.

6. A process according to Claim 1 wherein Y is NR* where R* independently each occurrence is selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof.

7. A process according to Claim 1 wherein M is titanium or zirconium.

8. A process according to Claim 7 wherein the metal coordination complex is (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane zirconium dichloride, (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane titanium dichloride, (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane zirconium dibenzyl, or (N-t-butylamido)(dimethyl)(η^5-2,3,4,5-tetramethylcyclopentadienyl)-silane titanium dibenzyl.

STATEMENT UNDER ARTICLE 19

Pursuant to Article 19, please amend Applicants' claims in the following manner.

Incorporate the limitations of previous claims 7 and 8 into claim 1.

Amend claim 3 to correct anide and phosphide to amine and phosphine respectively (next to last line).

Amend claims 3 and 4 to specify that M, m, L and q are as previously defined.

Renumber remaining claims and where necessary correct dependency.

New pages 12-14 containing the above changes are enclosed. Please substitute new pages 12-14 for pages 12-14 in the present application.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/08730

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07F7/28; C07F7/10; //C08F4/602C07F17/00
C08F10/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07F ; C08F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 420 436 (EXXON CHEMICAL PATENTS INC.) 3 April 1991 see the whole document ---	1,4-10
X	EP,A,0 418 044 (THE DOW CHEMICAL COMPANY) 20 March 1991 see the whole document ---	1,4-10
X	EP,A,0 416 815 (THE DOW CHEMICAL COMPANY) 13 March 1991 cited in the application see the whole document ---	1,4-10
P,X	WO,A,9 200 333 (EXXON CHEMICAL PATENTS INC.) 9 January 1992 see the whole document ---	1,4-10

-/--

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

1

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
08 DECEMBER 1992	21. 12. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	RINKEL L.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 67, 1967, Columbus, Ohio, US; abstract no. 44131f, MINSKER, K.S. ET AL. page 4163 ; see abstract & J. POLM. SCI., PART C NO. 16 (PT 3) 1967, pages 1489 - 1496	1-3

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9208730 SA 65999

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 08/12/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		AU-A-	6443990	18-04-91
		CA-A-	2024899	14-03-91
		CA-A-	2065745	14-03-91
		EP-A-	0491842	01-07-92
		JP-A-	3188092	16-08-91
		WO-A-	9104257	04-04-91
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WO-A-9200333	09-01-92	None		